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RAW MATERIALS

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SPECIFICS OF CLAYS FROM THE ANDREEVSKOE DEPOSIT

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Clay from the Andreevskoe deposit (Ukraine) is a high-quality material suitable for the ceramic industry for manufacturing a wide range of articles, from sewage pipes to high-strength insulators.

Argillaceous materials in Ukraine are known for their high quality not only in Europe but in the world. The clay from the Andreevskoe deposit is among the best materials (the license for mining this deposit belongs to VESKO JSC).

Following the classification scheme of the GOST 9169–59 standard, clays from the Andreevskoe deposit can be classified as basic (content of $Al_2O_3 + TiO_2$ after calcination 30 - 40%) and semi-acid (content of $Al_2O_3 + TiO_2$ after calcination 15 - 30%), refractory (heat resistance above 1580° C), and high-melting (heat resistance $1350 - 1580^{\circ}$ C) [1].

One of the most significant parameters of clay is the plasticity number. The plasticity of argillaceous materials depends on their mineralogical composition, dispersion, the particle shape and the state of the particle surface, and the presence of soluble salts. Tests performed using the Attenberg method at the Chair of Ceramics, Refractories, Glass, and Enamels of the Kharkov State Polytechnical University make it possible to attribute the clays from the Andreevskoe deposit to class I, since the plasticity number of all grades of clay exceeds 15: VESKO-Keramic — 15.6, VESKO-Granitik — 18.0, and VESKO-Prima — 20.8.

The content of the colorant oxides (Fe₂O₃ and TiO₂) points to the suitability of these clays for making light-colored (white) products, in particular, sanitaryware, porcelain, and faience. The sum of the colorant oxides in the VESKO-Extra and VESKO-Prima grades of Andreevskoe deposit clay does not exceed 2.5%. This is an extremely important parameter in the production of fine ceramics.

Several authors [1-4] note that soluble salts, namely, sulfates and chlorides, are undesirable impurities in clay. Unfortunately, nobody mentions the maximum permissible concentration of these salts. The content of chlorides and sulfates in Andreevskoe clay ranges within the following limits: $Cl^- - 0.1 - 0.3\%$, $SO_4^{2-} - 0.4 - 0.5\%$.

The studies performed at the Chair of Ceramics, Refractories, Glass, and Enamels of the Kharkov State Polytechnical University and in the Modena Centro Prove Laboratory (Italy) indicated that with respect to its mineralogical composition, clay from the Andreevskoe deposit belongs to polymineral (kaolinite-hydromica) clays. A high alumina content (up to 35-36%) points to the presence of the kaolinite group and the refractoriness of this materials. A rather high content of alkaline oxides (up to 2% K₂O) points to the presence of the illite (or hydromica) group and the capacity of the clay for early sintering while preserving its refractoriness. This is important for the firing technology, since the wider the sintering interval, the more stable is the article in firing. The article then is not deformed even when brought to full sintering. Andreevskoe clays of all grades have this important property (Table 1). The studies were carried out according to GOST 21216.9-93 and GOST 21216.11-93.

The dispersion and the granular composition of clay are of great significance in the production of ceramics. With respect to the content of coarse-grained inclusions, materials from the Andreevskoe deposit have a low content of such inclusions (not more than 1%), and the clays are finely-disperse (the content of particles below 1 µm in all grades of clay is above 60%). The studies were performed using the sieve method (for the coarse-dispersion fraction) and sedimentation method (for the finely-disperse fraction) based on GOSTs 21216.2–93, 21216.4–93, 21216.12–93, 3594.9–93,

TABLE 1

Parameter	Clay		
	VESKO-Prima	VESKO- Granitik	VESKO- Keramik
Refractoriness, °C Sintering interval, °C	1690 1050 – 1250	1630 1080 – 1250	1580 1130 – 1260

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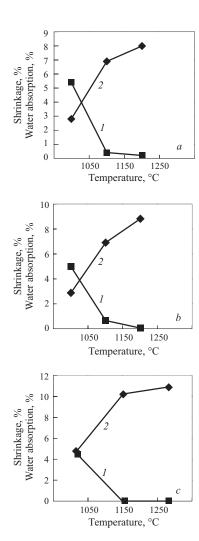


Fig. 1. Water absorption (1) and shrinkage (2) depending on sinterability in VESKO-Keramik (a), VESKO-Granitik (b) and VESKO-Prima (c) clays.

and 3594.12–93 at the Kharkov Technical University and at the Modena Centro Prove Laboratory. The clay contains virtually no minerals bearing S²- or SO $_4^2$ - anions ($S_{\rm tot} < 0.01\%$). This indicates that Andreevskoe clays contain nearly none of the toxic impurities such as pyrite FeS $_2$ and gypsum CaSO $_4 \cdot 2 \rm{H}_2 \rm{O}$.

Organic impurities are present in the majority of clays and tint them in colors ranging from gray to black. They have a dual effect on the technological properties of the clays. This is especially evident in relatively young clays, and Andreevskoe clays belong to the Upper Neogenic deposits [5]. On the one hand, the hydrophily of clays due to the presence of COOH, CO, and COH groups facilitates an increase in the hygroscopic moisture content and increases plasticity and cohesion. On the other hand, the presence of organic impurities in clay creates a local reducing medium in firing, which influences the transition of Fe³⁺ into Fe²⁺ and results in faster sintering of clays [1].

With a high amount of organic impurities ($C_{\rm tot} = 5\%$ or greater), humin compounds form a condensed structure phase that significantly modifies the properties of clay. Such phase may cause swelling and pore formation in clay firing. The value $C_{\rm tot}$ in Andreevskoe clays is only 0.1%, and the presence of organic impurities is not harmful, since they burn out in firing. This makes it possible to use clay from the Andreevskoe deposit in fast firing [6].

Thus, clays from the Andreevskoe deposit, according to the industrial classification, are white-burning, highly plastic, finely-disperse, with a wide sintering interval, and highly sinterable (water absorption up to 2%). Due to the absence of toxic impurities and a low content of organic impurities, such clays are suitable for fast firing.

Andreevskoe deposit clays can be widely used in production, from sewage pipes to high-strength insulators.

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